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L6: Entry 1 of 4 File: USPT Jul 6, 1993

DOCUMENT-IDENTIFIER: US 5225244 A
TITLE: Polymeric anti-reflection coatings and coated articles

Brief Summary Paragraph Right (3):
It has been well known for many years that unwanted reflections can be substantially reduced by providing a surface coating of an optically clear coating material having a refractive index which is lower than the refractive index of the substrate. However, difficulty in producing high quality thin films prevented significant practical application until approximately 1940, when the technology for the creation of thin films of various refractory inorganic materials via evaporation under high vacuum conditions was developed. In more recent times, low refractive index polymeric coatings, generally fluoropolymer coatings, have been provided for anti-reflection applications. Generally, these coatings, for maximum effectiveness, are about 1/4 wavelength thick. The basic theory of such anti-reflection coatings is well known; the technical challenge is in the provision of conveniently applied, effective, strongly adherent, scratch-resistant and relatively low cost coatings with optimally low refractive index.

Brief Summary Paragraph Right (4):
This invention provides devices comprising a reflective substrate having deposited thereon as an anti-reflection coating a thin film of copolymer of fluorine-containing acrylic monomers with non-fluorinated acrylic monomers. Such copolymer can be made under free-radical polymerization conditions. These copolymers are amorphous and optically clear, and have low refractive indexes. Being soluble in specific organic solvents, their solutions can be used to cast anti-reflection coatings, which can be cured by cross-linking. These coatings are strongly adherent to substrates, including glass, polymers, polymer films and crystal substrates. These copolymer anti-reflection coatings combine the superior properties of fluoropolymers--such as low refractive index and surface energy, good thermal and chemical resistance--with strong adhesion, flexibility, toughness, and abrasion resistance. Moreover, they can be easily applied from solution, and they are readily cured by cross-linking. They are suitable for application to very large area substrates at relatively low cost.

Brief Summary Paragraph Right (13):
These copolymers are generally optically clear, without haze or inhomogeneities. They have refractive indexes below about 1.4, generally within the range of from about 1.365 to below about 1.4; good adhesion to glass, silicon, copper foil, polyimide, nylon, polyethylene terephthalate, polytetrafluroethylene, polychlorotrifluoroethylene and other similar substrates; low surface energy, about half that of polytetrafluoroethylene; excellent thermal stability in air; in combination with good mechanical properties--they are neither brittle nor elastomeric. They are soluble (up to about 40 percent by weight of the combined weight of polymer and solvent) in about 1:1 THF/1,3-bis(trifluoromethyl)benzene (hereinafter also referred to as hexafluoroxylene). From such solutions, coatings can be applied to any suitable substrate, particularly optical substrates, such as glass, polymers, polymer films, crystals, and the like. Their dielectric constant is on the order of about 3.

Detailed Description Paragraph Right (45):
Most common eyeglass lenses are made out of glass (n=1.51) or a hard crosslinked polymer resin (n=1 51), although there is a move toward higher refractive index materials to reduce the required curvature. In both cases, the materials do not dissolve in any of the solvents used for the above-described polymer compositions. Both single layer and two layer anti-reflection coatings were applied to both types

of lenses via spin coating. Transmission spectra were taken for both uncoated and coated low positive diopter lenses. We observed about 97% transmission for a single layer coated lens and greater than 100% transmission for a two layer coated lens, both at their respective design wavelengths (the wavelength of minimum reflection). In comparison, an uncoated lens exhibited about 92.5% transmission. The percentages are slightly elevated relative to flat substrates due to lensing of the probe beam. There were negligible differences between the glass and resin lenses.

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L6: Entry 4 of 4 File: USPT Aug 18, 1992

DOCUMENT-IDENTIFIER: US 5139879 A
TITLE: Fluoropolymer blend anti-reflection coatings and coated articles

Abstract Paragraph Left (1):
Solid bodies having a reflective surface are provided with an anti-reflection coating of a fluoropolymer blends of (1) a terpolymer composition derived from (a) perfluoroalkylakyl acrylate or methacrylate, (b) acrylic, methacrylic or itaconic acid, and (c) hydroxyl- containing acrylate or methacrylate; and (2) an amorphous fluoropolymer.

Brief Summary Paragraph Right (3):
It has been well known for many years that unwanted reflections can be substantially reduced by providing a surface coating of an optically clear coating material having a refractive index which is lower than the refractive index of the substrate. However, difficulty in producing high quality thin films prevented significant practical application until approximately 1940, when technology for applying thin films of certain refractory inorganic materials via evaporation under high vacuum conditions was developed. More recently, low refractive index polymeric coatings, generally fluoropolymer coatings, have been developed for anti-reflection applications. Generally, these coatings, for maximum effectiveness, are about 1/4 wavelength thick. The basic theory of such anti-reflection coatings is well known; the technical challenge is in the provision of conveniently applied, effective, strongly adherent, scratch-resistant and relatively low cost coatings with optimally low refractive index, over large areas.

Brief Summary Paragraph Right (4):
This invention provides devices comprising a reflective substrate having deposited thereon as an anti-reflection coating a thin film of blends of (a) amorphous fluoropolymers with (b) certain cross-linkable terpolymers derived from fluorine-containing acrylic monomers with non-fluorinated acrylic monomers. These blends can be cured by application of heat to form semi-IPNs (interpenetrating networks) of the cured terpolymer which "trap" the amorphous fluoropolymer component. The cured blends remain amorphous, and they are optically clear. They are based on amorphous fluoropolymers containing only carbon and fluorine, and possibly hydrogen and/or oxygen, and they have low refractive indexes. Being soluble in specific organic solvents, solutions of the uncured blends can be used to make coatings and to cast films, which are cross-linkable. These coatings are optically clear, robust and strongly adherent to reflective substrates, including glass, polymer films, metals, crystal substrates and the like.

Brief Summary Paragraph Right (8):
The term copolymer, as used in the specification and claims, is intended to refer to a polymer derived from at least two or more, usually derived from at least three different monomer units. There is no theoretical limit on the number of different monomer units which may be incorporated into the fluorinated copolymers for the fluoropolymer blends for the anti-reflection coatings of the devices of the present invention; their number is limited only by the usual practical limitations imposed by polymerization process considerations, and the desire to obtain polymer products having useful properties. Sometimes, these copolymers are herein also referred to as terpolymers.

Brief Summary Paragraph Right (9):
The copolymer component for the fluoropolymer blends for the anti-reflection

coatings for the devices of the present invention may also be described as being made up of a polymer chain composed of

Brief Summary Paragraph Right (15):
These polymer blends are optically clear, without haze or inhomogeneities. They have refractive indexes below about 1.4, and as low as 1.327; good adhesion to glass, silicon, copper foil, polyimide, nylon, polyethylene terephthalate, polytetrafluoroethylene, polychlorotrifluoroethylene and other similar substrates; low surface energy, about half that of polytetrafluoroethylene; excellent thermal stability in air; in combination with good mechanical properties--they are neither brittle nor elastomeric.

Brief Summary Paragraph Right (19):
Anti-reflection coatings of the above-described fluoropolymer blends are conveniently applied to optical substrates, typically in 1/4 wavelength thickness, by coating the substrate with a solution of the blend, removing excess solution, if any, drying by evaporating the solvent, preferably, but not necessarily, followed by heat-treatment, as above described, to cure the coating by means of cross-linking. Typical substrates include optical lenses; eyeglasses, both plastic and glass; windows, glass as well as polymeric windows, such as windows of clear polymeric vinyl (incl. copolymers thereof), styrene, acrylics (Plexiglass) or polycarbonate (Lexan.RTM. supplied by General Electric); clear polymer films such as vinyl (incl. copolymers), nylon, polyester, and the like; the exterior viewing surface of liquid crystal displays, cathode ray tubes (e.g. video display tubes for televisions and computers); and the like; the surface of glossy displays and pictures, such as glossy prints and photographs; and the like. Determination of suitable coating thickness (generally 1/4 wavelength of the light of which reflection is to be minimized) is within the ordinary skill of the art, but is further elucidated, infra.

Detailed Description Paragraph Right (40):
A single layer anti-reflection coating of the composition 1:1 amorphous fluoropolymer (DuPont's Teflon.RTM. AF-1600) and the terpolymer product of Example 1 was applied to a 3 mm thick, 50 mm diameter Plexiglass disk in the above-described manner via spin coating from a 2.2 wt. % polymer blend solution in Fluorinert.RTM.FC-75 onto one side using spin rotation of 2000 rpm, followed by curing at 100.degree. C. for 30 minutes. The coating process was then repeated on the other side. Transmission spectra for both the coated and the uncoated disk are shown in FIG. 1. Significant enhancement of optical transmission is achieved by the coating.

Detailed Description Paragraph Right (41):
Most common eyeglass lenses are made out of glass (n=1.51) or a hard crosslinked polymer resin (n=1.51). In both cases, the materials do not dissolve in the solvents used for the above-described polymer compositions. Single layer anti-reflection coatings were applied to both types of lenses via dip coating, using .about.4 wt. % solution of 1:1 amorphous fluoropolymer (DuPont's Teflon.RTM.AF-1600) and terpolymer product of Example 1 in Fluorinert.RTM.FC-75. Transmission spectra were taken for both uncoated and coated low positive diopter lenses. We observed about 97.5% transmission for a single layer coated lens, while an uncoated lens exhibited about 91.5% transmission. There were negligible differences between the glass and resin lenses.

Detailed Description Paragraph Right (45):
A further effective application of the anti-reflection coated optical devices of the present invention involves their use as transparent covers for read-out instruments and instrument panels, such as automotive instrument panels. Such panels are commonly tilted, or curved, to reduce back reflected light. Tilting or curvature tend to reduce overall visibility, and to increase the size of the component. Application of an anti-reflection coating of the above-described fluoropolymer blend composition effectively reduces reflection and increases instrument visibility.

CLAIMS:

14. An anti-reflection coated solid body according to claim 13 wherein the fluoropolymer in said second layer is cross-linked.

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L6: Entry 3 of 4 File: USPT Jan 12, 1993

DOCUMENT-IDENTIFIER: US 5178955 A
TITLE: Polymeric anti-reflection coatings and coated articles

Brief Summary Paragraph Right (3):
It has been well known for many years that unwanted reflections can be substantially reduced by providing a surface coating of an optically clear coating material having a refractive index which is lower than the refractive index of the substrate. However, difficulty in producing high quality thin films prevented significant practical application until approximately 1940, when the technology for the creation of thin films of various refractory inorganic materials via evaporation under high vacuum conditions was developed. In more recent times, low refractive index polymeric coatings, generally fluoropolymer coatings, have been provided for anti-reflection applications. Generally, these coatings, for maximum effectiveness, are about 1/4 wavelength thick. The basic theory of such anti-reflection coatings is well known; the technical challenge is in the provision of conveniently applied, effective, strongly adherent, scratch-resistant and relatively low cost coatings with optimally low refractive index.

Brief Summary Paragraph Right (4):
This invention provides devices comprising a reflective substrate having deposited thereon as an anti-reflection coating a thin film of copolymer of fluorine-containing acrylic monomers with non-fluorinated acrylic monomers. Such copolymer can be made under free-radical polymerization conditions. These copolymers are amorphous and optically clear, and have low refractive indexes. Being soluble in specific organic solvents, their solutions can be used to cast anti-reflection coatings, which can be cured by cross-linking. These coatings are strongly adherent to substrates, including glass, polymers, polymer films and crystal substrates. These copolymer anti-reflection coatings combine the superior properties of fluoropolymers--such as low refractive index and surface energy, good thermal and chemical resistance--with strong adhesion, flexibility, toughness, and abrasion resistance. Moreover, they can be easily applied from solution, and they are readily cured by cross-linking. They are suitable for application to very large area substrates at relatively low cost.

Brief Summary Paragraph Right (10):
These copolymers are generally optically clear, without haze or inhomogeneities. They have refractive indexes below about 1.4, generally within the range of from about 1.365 to below about 1.4; good adhesion to glass, silicon, copper foil, polyimide, nylon, polyethylene terephthalate, polytetrafluroethylene, polychlorotrifluoroethylene and other similar substrates; low surface energy, about half that of polytetrafluoroethylene; excellent thermal stability in air; in combination with good mechanical properties--they are neither brittle nor elastomeric. They are soluble (up to about 40 percent by weight of the combined weight of polymer and solvent) in about 1:1 THF/1,3-bis(trifluoromethyl)benzene (hereinafter also referred to as hexafluoroxylene). From such solutions, coatings can be applied to any suitable substrate, particularly optical substrates, such as glass, polymers, polymer films, crystals, and the like. Their dielectric constant is on the order of about 3.

Detailed Description Paragraph Right (45):
Most common eyeglass lenses are made out of glass (n=1.51) or a hard crosslinked polymer resin (n=1.51), although there is a move toward higher refractive index materials to reduce the required curvature. In both cases, the materials do not dissolve in any of the solvents used for the above-described polymer compositions. Both single layer and two layer anti-reflection coatings were applied to both types

of lenses via spin coating. Transmission spectra were taken for both uncoated and coated low positive diopter lenses. We observed about 97% transmission for a single layer coated lens and greater than 100% transmission for a two layer coated lens, both at their respective design wavelengths (the wavelength of minimum reflection). In comparison, an uncoated lens exhibited about 92.5% transmission. The percentages are slightly elevated relative to flat substrates due to lensing of the probe beam. There were negligible differences between the glass and resin lenses.

CLAIMS:

12. An anti-reflection coated solid body according to claim 11 wherein the fluoropolymer in said second layer is cross-linked.

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L6: Entry 2 of 4 File: USPT Mar 30, 1993

DOCUMENT-IDENTIFIER: US 5198267 A
TITLE: Fluoropolymer blend anti-reflection coatings and coated articles

Abstract Paragraph Left (1):
Solid bodies having a reflective surface are provided with an anti-reflection coating of a fluoropolymer blends of (1) a terpolymer composition derived from (a) perfluoroalkylalkyl acrylate or methacrylate, (b) acrylic, methacrylic or itaconic acid, and (c) hydroxyl-containing acrylate or methacrylate; and (2) an amorphous fluoropolymer.

Brief Summary Paragraph Right (3):
It has been well known for many years that unwanted reflections can be substantially reduced by providing a surface coating of an optically clear coating material having a refractive index which is lower than the refractive index of the substrate. However, difficulty in producing high quality thin films prevented significant practical application until approximately 1940, when technology for applying thin films of certain refractory inorganic materials via evaporation under high vacuum conditions was developed. More recently, low refractive index polymeric coatings, generally fluoropolymer coatings, have been developed for anti-reflection applications. Generally, these coatings, for maximum effectiveness, are about 1/4 wavelength thick. The basic theory of such anti-reflection coatings is well known; the technical challenge is in the provision of conveniently applied, effective, strongly adherent, scratch-resistant and relatively low cost coatings with optimally low refractive index, over large areas.

Brief Summary Paragraph Right (4):
This invention provides devices comprising a reflective substrate having deposited thereon as an anti-reflection coating a thin film of blends of (a) amorphous fluoropolymers with (b) certain cross-linkable terpolymers derived from fluorine-containing acrylic monomers with non-fluorinated acrylic monomers. These blends can be cured by application of heat to form semi-IPNs (interpenetrating networks) of the cured terpolymer which "trap" the amorphous fluoropolymer component. The cured blends remain amorphous, and they are optically clear. They are based on amorphous fluoropolymers containing only carbon and fluorine, and possibly hydrogen and/or oxygen, and they have low refractive indexes. Being soluble in specific organic solvents, solutions of the uncured blends can be used to make coatings and to cast films, which are cross-linkable. These coatings are optically clear, robust and strongly adherent to reflective substrates, including glass, polymer films, metals, crystal substrates and the like.

Brief Summary Paragraph Right (10):
The term copolymer, as used in the specification and claims, is intended to refer to a polymer derived from at least two or more, usually derived from at least three different monomer units. There is no theoretical limit on the number of different monomer units which may be incorporated into the fluorinated copolymers for the fluoropolymer blends for the anti-reflection coatings of the devices of the present invention; their number is limited only by the usual practical limitations imposed by polymerization process considerations, and the desire to obtain polymer products having useful properties. Sometimes, these copolymers are herein also referred to as terpolymers.

Brief Summary Paragraph Right (11):
The copolymer component for the fluoropolymer blends for the anti-reflection coatings for the devices of the present invention may also be described as being made up of a polymer chain composed of

Brief Summary Paragraph Right (17):
These polymer blends are optically clear, without haze or inhomogeneities. They have refractive indexes below about 1.4, and as low as 1.327; good adhesion to glass, silicon, copper foil, polyimide, nylon, polyethylene terephthalate, polytetrafluoroethylene, polychlorotrifluoroethylene and other similar substrates; low surface energy, about half that of polytetrafluoroethylene; excellent thermal stability in air; in combination with good mechanical properties--they are neither brittle nor elastomeric.

Brief Summary Paragraph Right (21):
Anti-reflection coatings of the above-described fluoropolymer blends are conveniently applied to optical substrates, typically in 1/4 wavelength thickness, by coating the substrate with a solution of the blend, removing excess solution, if any, drying by evaporating the solvent, preferably, but not necessarily, followed by heat-treatment, as above described, to cure the coating by means of cross-linking. Typical substrates include optical lenses; eyeglasses, both plastic and glass; windows, glass as well as polymeric windows, such as windows of clear polymeric vinyl (incl. copolymers thereof), styrene, acrylics (Plexiglass) or polycarbonate (Lexan.RTM. supplied by General Electric); clear polymer films such as vinyl (incl. copolymers), nylon, polyester, and the like; the exterior viewing surface of liquid crystal displays, cathode ray tubes (e.g. video display tubes for televisions and computers); and the like; the surface of glossy displays and pictures, such as glossy prints and photographs; and the like. Determination of suitable coating thickness (generally 1/4 wavelength of the light of which reflection is to be minimized) is within the ordinary skill of the art, but is further elucidated, infra.

Detailed Description Paragraph Right (39):
A single layer anti-reflection coating of the composition 1.1 amorphous fluoropolymer (DuPont's Teflon.RTM. AF-1600) and the terpolymer product of Example 1 was applied to a 5 mm thick, 50 mm diameter Plexiglass disk in the above-described manner via spin coating from a 2.2 wt.% polymer blend solution in Fluorinert.RTM. FC-75 onto one side using spin rotation of 2000 rpm, followed by curing at 100.degree. C. for 30 minutes. The coating process was then repeated on the other side. Transmission spectra for both the coated and the uncoated disk are shown in FIG. 1. Significant enhancement of optical transmission is achieved by the coating.

Detailed Description Paragraph Right (40):
Most common eyeglass lenses are made out of glass (n=1.51) or a hard crosslinked polymer resin (n=1.51). In both cases, the materials do not dissolve in the solvents used for the above-described polymer compositions. Single layer anti-reflection coatings were applied to both types of lenses via dip coating, using .about.4 wt.% solution of 1:1 amorphous fluoropolymer (DuPont's Teflon.RTM. AF-1600) and terpolymer product of Example 1 in Fluorinert.RTM. FC-75. Transmission spectra were taken for both uncoated and coated low positive diopter lenses. We observed about 97.5% transmission for a single layer coated lens, while an uncoated lens exhibited about 91.5% transmission. There were negligible differences between the glass and resin lenses.

Detailed Description Paragraph Right (44):
A further effective application of the anti-reflection coated optical devices of the present invention involves their use as transparent covers for read-out instruments and instrument panels, such as automotive instrument panels. Such panels are commonly tilted, or curved, to reduce back reflected light. Tilting or curvature tend to reduce overall visibility, and to increase the size of the component. Application of an anti-reflection coating of the above-described fluoropolymer blend composition effectively reduces reflection and increases instrument visibility.